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A New Derivation of the Virial Expansion

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To overcome the mathematical complexity on the one hand or the lack of rigor on the other in usual treatments of the virial expansion, a new derivation is presented. This derivation, while simple and mathematically valid, clearly illustrates the most important features of the cluster expansion derivation of the second and third virial coefficients. Thus it is expected to be of use in statistical mechanics courses.

I. INTRODUCTION

In presenting the problem of the classical imperfect gas to graduate statistical mechanics classes, I have often been annoyed that there was no transparent way to show the various features of the theory. To derive the virial expansion rigorously requires mathematical complexity which is usually too much for any class to bear. On the other hand, a well-known simple derivation of the second virial coefficient as reviewed below, is so mathematically questionable for large N, that one hesitates to present it. To overcome these difficulties of mathematical complexity or lack of rigor, I have developed a technique that also illustrates very nicely most of the salient features of the cluster expansion method.

To introduce notation, let me review the imperfect gas problem briefly. The free energy can be written as

$$F=F_{\text{ideal}}+F_c=-kT\ln Z_{\text{ideal}}-kT\ln Z_c, \quad (1)$$

where F_{ideal} and Z_{ideal} are the free energy and partition function of the ideal gas, and F_c and Z_c are the configurational free energy and partition function. The latter is defined by

$$Z_c=(V^N)^{-1}\int\prod_{i<j}(1+f_{ij})d\mathbf{r}_1d\mathbf{r}_2\cdots d\mathbf{r}_N, \quad (2)$$

where

$$f_{ij}=f(r_{ij})=\exp[-v(r_{ij})/kT]-1, \quad (3)$$

V is the volume, N is the number of particles in the system, and $v(r_{ij})$ is the pair potential.

The virial expansion for the pressure is

$$P=P_{\text{ideal}}+P_c=-(\partial F_{\text{ideal}}/\partial V)-(\partial F_c/\partial V)$$
$$=(NkT/V)(1+\rho B+\rho^2 C+\cdots), \quad (4)$$

where B, C, $\cdots$ are the second, third, $\cdots$ virial coefficients.

In the Ursell–Mayer[1,2] expansion one writes

$$\prod_{i<j}(1+f_{ij})=1+\sum_{i<j}f_{ij}+\sum\sum f_{ij}f_{kl}+\cdots. \quad (5)$$

This expansion is integrated term by term; the structure and number of each kind of term is analyzed and resummed according to Mayer's theorem[2] to get a form for Z_c. This Z_c is then used in the grand partition function to develop an expression for the pressure P. The analysis is so involved mathematically that I suspect few teachers of statistical mechanics actually present it in class. Although most textbooks cover this derivation, I would guess that not many students take the trouble to go through it, and those that do miss much of the physical insights because of the mathematical complications. This condition is indeed unfortunate since this cluster expansion is such a classic illustration of a fundamental method of many-body physics.

One standard oversimplified method[1,3] of presenting the imperfect gas problem is to truncate the expansion (4) after the one$-f$ term and write

$$Z_c\cong 1+[N(N-1)/2V]\bar{f}, \quad (6)$$

where

$$\bar{f}=\int f(\mathbf{r})\,d\mathbf{r}. \quad (7)$$

Neglecting a term $O(N^0)$ we have

$$Z_c\cong 1+\tfrac{1}{2}(N\rho)\bar{f}, \quad (8)$$

where the density is

$$\rho=N/V. \quad (9)$$

The configurational free energy is

$$F_c=-kT\ln Z_c=-kT\ln[1+\tfrac{1}{2}(N\rho)\bar{f}]. \quad (10)$$

Since ρ is small, we expand the logarithm and keep one term, to give

$$F_c=-kTN\rho\bar{f}.$$

This result gives the correct expression for the pressure to first order in ρ. However, the derivation involves a lot of hand waving and eye winking. For one thing, why drop the term of order N in Expression (6) to get to Expression (8) and yet keep the leading unity? Indeed, by truncating the series after the one$-f$ terms, one neglects terms of order N^2, N^3, etc. Secondly, the truncated expansion of the logarithm is hardly valid since $\frac{1}{2}(N\rho)\bar{f}$ is not small, but $O(N)$.

This derivation, even if it could be tightened up mathematically, is not satisfying because it does not really carry much of the flavor of the true cluster expansion technique.

There are some methods that are not so very complicated mathematically and that lead rigorously to the virial expansion. One of these is the Van Kampen[4] cluster expansion, in which one considers Z_c to be an average value. Then the average of the product is approximated by the product of the averages, namely,

$$Z_c=\langle\prod_{i<j}(1+f_{ij})\rangle=\prod_{i<j}\langle(1+f_{ij})\rangle. \quad (11)$$

This method leads quickly to the virial expansion accurate to first order in ρ. It can be corrected in a straightforward way to arrive at higher orders in ρ. As nice a technique as this is, I find it a bit difficult to justify *a priori* to a class that the approximation (11) is expected to lead to the lowest order corrections in the density. In this method in higher order one never sees the reducible clusters at all, which may be a blessing or a misfortune, depending on your point of view.

There is also a derivation given by Landau and Lifshitz[5] that seems mathematically correct and not overwhelmingly difficult. Since this text is easily available to most readers, I will not discuss the derivation here. The reader can best judge its suitability for himself.

My own derivation has the following attributes:

(a) it illustrates and overcomes the problem associated with the fact that the expansion Eq. (5) is a series in powers of N;

(b) it is a mathematically correct derivation;
(c) it illustrates the cancellation of the reducible diagrams; and
(d) both the second and third virial coefficient are derived in a simple manner.

II. DERIVATION

We integrate Eq. (5) term by term to give us Z_c in terms of the integrals represented diagrammatically as

$$(-) = V^{-1}\int f_{12}d\tau_{12}, \tag{12}$$

where

$$d\tau_{1\cdots n} = d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_n, \tag{13}$$

$$(<) = V^{-1}\int f_{12}f_{23}d\tau_{123}, \tag{14}$$

$$(=) = (V^2)^{-1}\int f_{12}f_{34}d\tau_{1234}, \tag{15}$$

$$(\triangle) = V^{-1}\int f_{12}f_{23}f_{31}d\tau_{123}, \tag{16}$$

$$(\sqsubset) = V^{-1}\int f_{12}f_{23}f_{34}d\tau_{1234}, \tag{17}$$

$$(\lessdot) = V^{-1}\int f_{12}f_{13}f_{14}d\tau_{1234}, \tag{18}$$

$$(\leq) = (V^2)^{-1}\int f_{12}f_{23}f_{45}d\tau_{1\cdots 5}, \tag{19}$$

$$(\equiv) = (V^3)^{-1}\int f_{12}f_{34}f_{56}d\tau_{1\cdots 6}, \tag{20}$$

etc.

Each integral is defined with the appropriate volume factors so it is of order unity. These integrals are clearly all the possible one, two, and three $-f$ terms that occur in Z_c. We have, up to the three $-f$ terms,

$$\begin{aligned} Z_c = \Bigg(1 &+ \frac{N!}{(N-2)!2!}V^{-1}(-) \\ &+ \frac{N!}{(N-3)!2!}(V^2)^{-1}(<) \\ &+ \frac{N!}{(N-4)!(2!)^3}(V^2)^{-1}(=) \\ &+ \frac{N!}{(N-3)!3!}(V^2)^{-1}(\triangle) \\ &+ \frac{N!}{(N-4)!2!}(V^3)^{-1}(\sqsubset) \\ &+ \frac{N!}{(N-4)!3!}(V^3)^{-1}(\lessdot) \\ &+ \frac{N!}{(N-5)!(2!)^2}(V^3)^{-1}(\leq) \\ &+ \frac{N!}{(N-6)!(2!)^3 3!}(V^3)^{-1}(\equiv) + \cdots\Bigg). \end{aligned} \tag{21}$$

The multiplication factors are the number of times each integral occurs in the Z_c series. They are easily derived by the usual combinatorial techniques with which most statistical mechanics students are familiar. It is evident that this series contains terms to all orders in N, despite the fact that $\ln Z_c$ must be $O(N)$.

We see how such a situation arises in the next step of the derivation in which we use a technique analogous to that introduced by Opechowski[6] in his treatment of high temperature expansions for spin systems. Since the virial expansion is a power series in the density, we certainly expect to be able to write the configurational free energy as a power series in V^{-1}:

$$F_c = NkT\sum_{n=0}^{\infty} A_n \frac{N^n}{V^n}. \tag{22}$$

We have included an explicit factor of N since F_c is extensive; the factor of kT is for convenience.

From Eq. (1) we can write

$$\begin{aligned} Z_c &= \exp(-F_c/kT) \\ &= \exp\Big[-N\sum_n A_n(N^n/V^n)\Big]. \end{aligned} \tag{23}$$

Next expand this exponential to give

$$\begin{aligned} Z_c = 1 &- N\left(A_0 + \frac{N}{V}A_1 + \frac{N^2}{V^2}A_2 + \cdots\right) \\ &+ \frac{N^2}{2!}\left(A_0 + \frac{N}{V}A_1 + \frac{N^2}{V^2}A_2 + \cdots\right)^2 + \cdots \\ = 1 &+ (-NA_0 + \tfrac{1}{2}N^2A_0^2 + \cdots) \\ &+ V^{-1}(-N^2A_1 + N^3A_0A_1) \\ &+ (V^2)^{-1}(-N^3A_2 + \tfrac{1}{2}N^4A_1^2 + N^4A_0A_2) + \cdots. \end{aligned} \tag{24}$$

This series is clearly a series in various powers of N, even though F_c was a well-behaved function of order N. We can find the values for the A_n by identifying coefficients of the various powers of V^{-1} in Eq. (24) with those in Eq. (21). We find

$$A_0=0, \tag{25}$$

$$A_1=-[N!/N^2(N-2)!2!](-), \tag{26}$$

$$A_2=-(N^3)^{-1}\left(\frac{N!}{(N-3)!3!}(\triangle)+\frac{N!}{(N-3)!2!}(<)\right.$$
$$\left.+\frac{N!}{(N-4)!(2!)^3}(=)-\tfrac{1}{2}N^4A_1^2\right). \tag{27}$$

We make use of the fact that $(<)$ is a "reducible" diagram, i.e., that

$$(<)=(=). \tag{28}$$

Also note that

$$(-)^2=(=). \tag{29}$$

This leads to partial cancellation of the last three terms in Eq. (27). By expanding out the factors in N we find

$$A_2=-(N^3)^{-1}\{[N!/(N-3)!3!](\triangle)$$
$$-\tfrac{1}{4}N(N-1)(=)\}. \tag{30}$$

In the thermodynamic limit of

$$N\to\infty, \quad V\to\infty, \quad \rho=N/V=\text{const}, \tag{31}$$

the coefficients become

$$A_1=-\tfrac{1}{2}(-), \tag{32}$$

$$A_2=-\tfrac{1}{6}(\triangle). \tag{33}$$

In this limit the reducible diagram and disconnected diagrams disappear completely, and the coefficients are $O(1)$ as we assumed in writing Eq. (22).

The pressure is obtained from Eq. (4). With Eq. (22) we see the configurational contribution to P is

$$P_c=kT\sum_{n=1}^{\infty}nA_n\frac{N^{n+1}}{V^{n+1}}$$
$$=kT\rho(A_1\rho+2A_2\rho^2+\cdots) \tag{34}$$

or

$$P=(NkT/V)(1+A_1\rho+2A_2\rho^2+\cdots). \tag{35}$$

Thus A_1 and $2A_2$, Eqs. (32) and (33), are the second and third virial coefficients, respectively.

The derivation does not provide a general expression for the virial coefficients, nor does it prove generally that reducible diagrams always cancel, and of course, this has not been its purpose. It does give the student a clear picture of the various properties of the cluster expansion, so that if he choses to examine a general treatment he will understand its significance.

If a teacher of statistical mechanics still does not wish to go into the discussion of the reducible diagrams or the third virial coefficient, this derivation also offers the possibility of truncation of the series Eqs. (21) and (24) after just the term in $1/V$ to arrive at a very easy and valid derivation of just the second virial coefficient.

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